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## Electrochemical gating-induced reversible and drastic resistance switching in VO<sub>2</sub> nanowires

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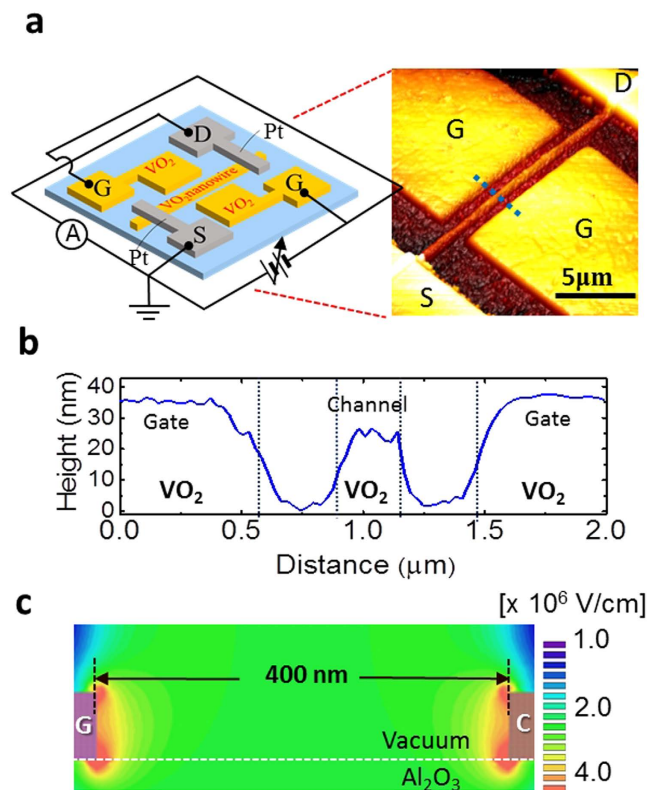
Reversible and drastic modulation of the transport properties in vanadium dioxide (VO<sub>2</sub>) nanowires by electric field-induced hydrogenation at room temperature was demonstrated using the nanogaps separated by humid air in field-effect transistors with planer-type gates (PG-FET). These PG-FETs allowed us to investigate behavior of revealed hydrogen intercalation and diffusion aspects with time and spatial evolutions in nanowires. These results show that air nanogaps can operate as an electrochemical reaction field, even in a gaseous atmosphere, and offer new directions to explore emerging functions for electronic and energy devices in oxides.

The transport characteristics of transition metal oxides are sensitive to redox reactions because the valence numbers of the transition metal ions are easily changed by the reactions, which affect the carrier density and/or stabilization of the crystal structure<sup>1–4</sup>. Of the prototypical materials, VO<sub>2</sub> is promising as it undergoes a metal-insulator transition (MIT) and the resistance changes by orders of magnitude around 340 K. In VO<sub>2</sub> nano to microstructures<sup>5–13</sup>, the coupling of the MIT with mechanical<sup>7–9</sup>, optical<sup>13</sup>, thermal<sup>12</sup> and electronic properties<sup>9,11</sup> can be used in tunable resonators, optical switchers, electronic and thermo-sensing devices. Furthermore, only a few atomic percent of the hydrogen- or oxygen-intercalation and -desorption in VO<sub>2</sub> cause drastic changes in the transport properties, equal to that caused by inducing the MIT<sup>14–20</sup>. Conventionally, controlling the amount of hydrogen/oxygen ions in an oxide has been conducted by annealing the samples under redox gas atmospheres<sup>1,4,15,16</sup>, in an aqueous solution<sup>17,18</sup> and with a hydrogen spillover method<sup>14,19</sup>. Every method requires high temperatures of at least 150 °C. Recently, on the other hand, an electric field has been shown to be a means of both hydrogenation and oxidization in oxides at room temperature<sup>20–23</sup>. For example, a strong electric field in ionic liquid (IL) gates induces oxygen vacancy formation in VO<sub>2</sub><sup>22</sup>. In IL or CAN (amorphous 12CaO·7Al<sub>2</sub>O<sub>3</sub> with a nanoporous structure) gates including water<sup>21,24</sup>, furthermore, hydrogen ions can be intercalated by positive electric field. Thus electrochemical gating including water electrolysis has a full potential to allow tuning of doping level at room temperature. In this paper, we report investigation of systematic transport modulation in VO<sub>2</sub> nanowires by electrochemical gating *via* air gap under humid condition and establishment of the ion diffusion model, giving the hydrogen ion intercalation and diffusion aspects with time and spatial evolutions in VO<sub>2</sub>.

### Results

**Proposed device structure.** As a proper device structure to perform this experiment, we have prepared planer-type field effect transistor with side gates and a nanoscaled wire channel separated by air nanogaps (PG-FET) illustrated in Fig. 1a. This type of device has following advantages: An electric field can be applied under various different gas and vapor atmospheres through the air nanogap. In this study, air with various humidity levels and dry air were used. Secondly, the electric-field induced ion intercalation and diffusion aspects with the time and spatial evolutions in the vicinity of interface can be systematically investigated because ions are intercalated from channel edges of both side and diffuse

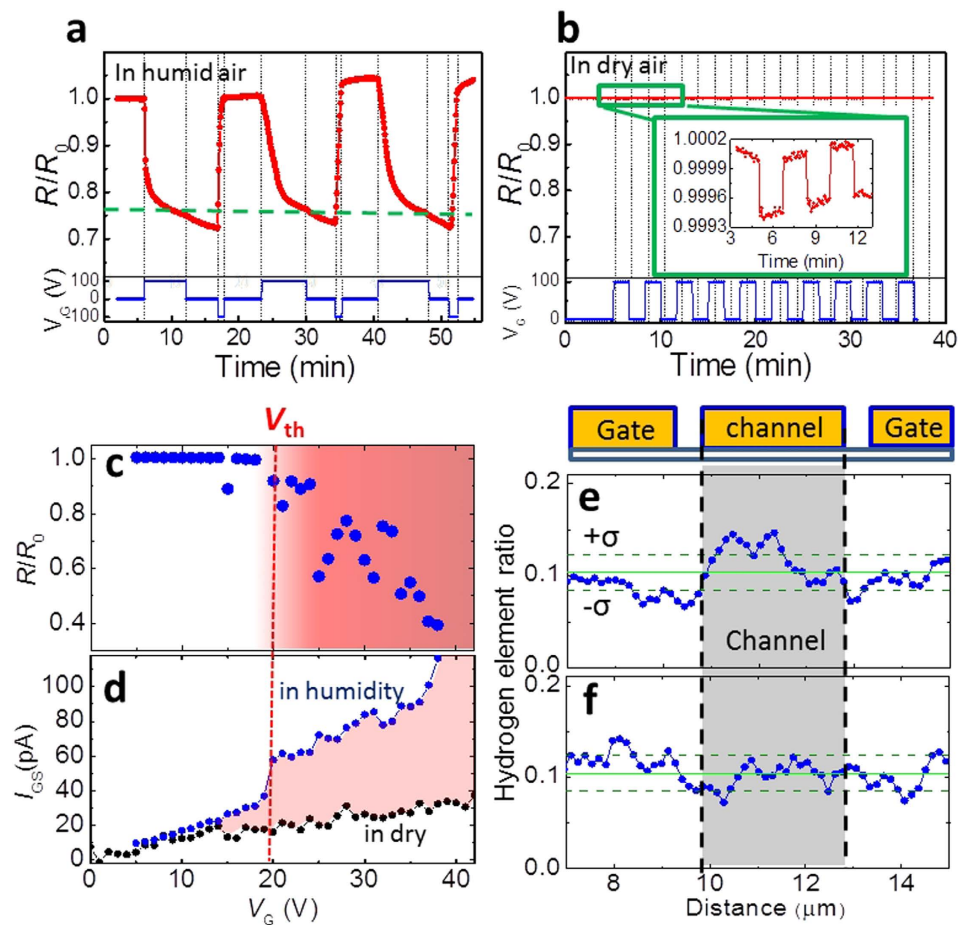
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**Figure 1.** VO<sub>2</sub> nanowire device with planer-type gates. (a) The typical device architecture and an atomic force microscope (AFM) image of the VO<sub>2</sub> channel area. S, D and G indicate the source, drain and gate electrodes, respectively. (b) Cross-sectional AFM image, taken at the blue dashed line in (a). (c) Cross-sectional electric field map, determined using finite element analysis at  $V_G = 100$  V through the 400-nm vacuum gap between G and the channel (c) on an Al<sub>2</sub>O<sub>3</sub> substrate under vacuum.

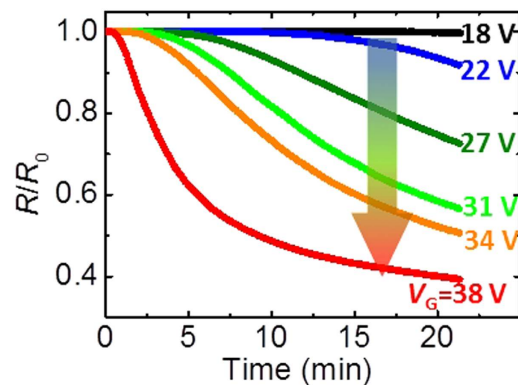
from the sides in VO<sub>2</sub>. Especially a narrower channel often enhances interface effect. An atomic force microscope image of a device is shown in Fig. 1a and the height profile is in Fig. 1b. The thicknesses of the channels and the gap distance were roughly 35 nm and 400 nm, respectively. The channel widths ( $w$ ) were systematically changed from 3 μm to 400 nm (see Methods and Supplementary Information section A for details). Figure 1c shows a cross-sectional electric field map, obtained using a Finite Element simulation using typical experimental parameters (see Supplementary Information section B). The electric field converged at the edges of the channels, providing the strongest effect on the electrochemical reactions. Thus the field-induced ion intercalation begins at the lateral sides of the nanowires

**Drastic resistance modulation by electrochemical induced-hydrogenation.** Figure 2a shows the reversible and non-volatile resistance modulation in a VO<sub>2</sub> nanowire channel ( $w = 500$  nm), found by applying a positive and negative  $V_G$  at 300 K under a humidity of around 50%. The normalized resistance ( $R/R_0$ ), where  $R$  and  $R_0$  are the resistance and the pristine resistance before applying a  $V_G$  at 300 K, respectively, slowly continued to drop during the application of  $V_G = +100$  V down to the saturation line at roughly  $R/R_0 = 0.75$ . This state was held after removal of the  $V_G$ . Namely, it exhibited a non-volatile memory effect. In contrast, the resistance increased again at  $V_G = -100$  V. Regarding slow resistive drops by an electric field, it is suggested that the origin would be related to mechanical relaxation or slow traps according to some reports<sup>25–27</sup>. In our PG-FET devices, on the other hand, such slow changes in the resistance were not observed under dry air condition (Fig. 2b). A steep resistance-switching of 0.06% occurred without any non-volatile memory effects, as shown in the inset of Fig. 2b. Approximately  $10^{12}$  cm<sup>-2</sup> electrons should be accumulated at  $V_G = 100$  V and 400 nm-gap distance. From Hall measurements in VO<sub>2</sub> thin films on Al<sub>2</sub>O<sub>3</sub> substrates<sup>28</sup>, the carrier density was evaluated at  $\sim 4 \times 10^{18}$  cm<sup>-3</sup>, equivalent to the Debye length of  $\sim 2$  nm. Given modulation of resistivity in both lateral sides in our device geometry, the calculated modulation rate would be ideally 0.4%. Thus, it is considered that a pure carrier accumulation acts at lateral sides in dry air condition though the efficiency on the electrostatic effects was not so high compared with the ideal case. From the presence of the steep resistive switching in Fig. 2b, the origin of slow resistive drops under humid air conditions is not likely to attribute to the mechanical relaxation or slow traps as mentioned above, but rather to electrochemical reaction with intercalation of hydrogen ions<sup>21,24,27,29</sup>, which can significantly reduce resistivity in 3d-orbital sensitive systems<sup>30</sup> (see Supplementary



**Figure 2.** Effect of the electric field on the transport properties and hydrogen intercalations in a  $\text{VO}_2$  channel. (a,b) Time dependence of the normalized resistance ( $R/R_0$ , where  $R_0$  is the pristine resistance of a non-treated  $\text{VO}_2$  channel at 300 K with applied  $V_G$  values of 100, 0 and  $-100$  V) (a) in humid air and (b) in dry air. The green dashed line in (a) indicates the rough saturation of  $R/R_0$ . The inset in (b) is a magnified view. (c)  $V_G$  dependence of  $R/R_0$  after applying a  $V_G$  for 20 minutes. (d)  $V_G$  dependence of the current between the gate and source electrodes ( $I_{GS}$ ) under a humidity of 60% (blue dotted-line) and in dry air (black line). (e,f) The relative elemental ratios for hydrogen normalized by oxygen (e) in a device after applying  $V_G = 100$  V and (f) in a pristine device. The solid and dashed green lines represent the averages of the hydrogen atom profiles and the standard deviations, respectively.

Information C for the intercalation ( $V_G = 100$  V) and non-intercalation ( $V_G = 0$  V) cases in detail) and/or color-switching properties known as electrochromism<sup>31</sup>. In  $\text{VO}_2$  intercalated hydrogen ions, a strong H-O bond induces electron transfer from hydrogen onto the oxygen atom, resulting in higher  $3d$ -orbital occupancy of vanadium from  $\text{V}^{4+}(3d^1)$  to  $\text{V}^{3+}(3d^2)$ <sup>5</sup>. Figure 2c shows  $V_G$  dependence of  $R/R_0$  20 minutes after applying the  $V_G$  to investigate the magnitude of resistance changes with variety of  $V_G$ . The threshold voltage starting to the reduction ( $V_{th}$ ) was approximately 20 V and the magnitude of the resistance changes was enhanced with increasing  $V_G$ . The resistance fluctuation in over 20 V would be due to fluctuation for level of humidity. The resistance modulation is sensitive to the level of humidity. In addition, repetitive intercalation and desorption of hydrogen ions may slightly change crystallinity of  $\text{VO}_2$  channels, causing the resistive fluctuation. In response with the resistance changes, the current between the gate and source electrodes ( $I_{GS}$ ) suddenly increased at around 20 V as seen in Fig. 2d, corresponding to the  $V_{th}$  in Fig. 2c. Subtracting the current recorded under humid conditions from that recorded under dry conditions gives the current generated by the electrolysis of water. Accordingly, the density of generated hydrogen ions increases with increasing  $V_G$  and the number of intercalated hydrogen ions in  $\text{VO}_2$  increases. Additionally, Fig. 2e shows the ratio of hydrogen elements in a device after applying  $V_G = 100$  V, investigated by ToF-SIMS (time-of-flight secondary ion mass spectrometer). It can be indicated that hydrogen content in  $\text{VO}_2$  channel is higher than that in other area in a device after applying the  $V_G$ , though the hydrogen content is roughly averaged because spatial resolution in the measurement is several hundred nanometer at most, whereas the hydrogen contents remain unchanged in a pristine device in Fig. 2f (see Supplementary Information section D in detail).



**Figure 3.** Transport properties from redox reactions in VO<sub>2</sub> by the electrolysis of water with various  $V_G$  values. Time dependence of  $R/R_0$  for different  $V_G$  values under a humidity of 60% at 300 K.

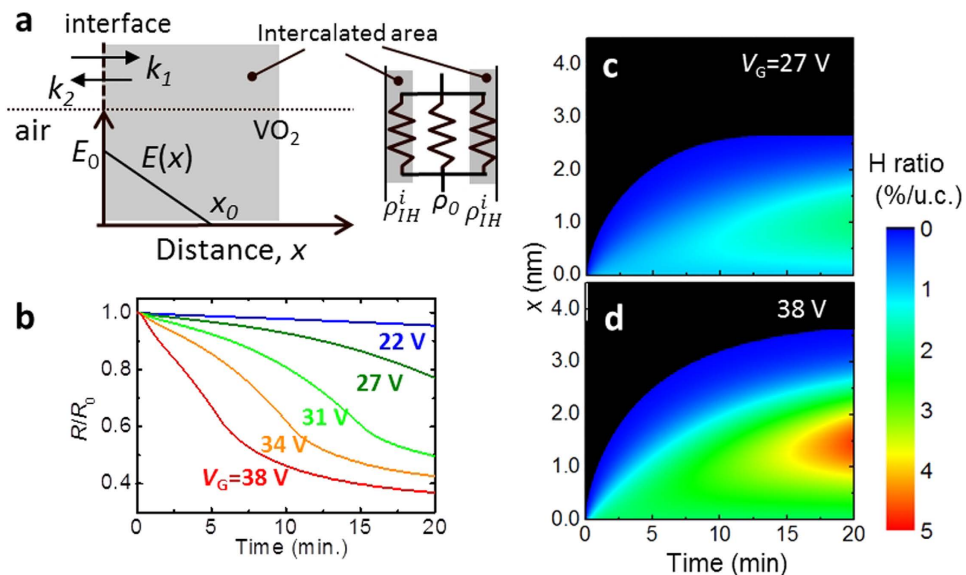
**Establishment in ion diffusion model by electrochemical gating.** It is known that a 1% hydrogen intercalation per VO<sub>2</sub> unit cell induces almost one order of magnitude reduction in resistivity<sup>17,18</sup>. Based on the empirical facts and the intercalation from the channel edge by applying electric gate from lateral sides, the amount of intercalated hydrogen ions and the effect on the diffusive aspect in VO<sub>2</sub> can be evaluated by investigating the resistive behavior with a variety of  $V_G$  values. Figure 3 shows the time dependence of the resistive modulations with various  $V_G$  under a humidity of 60%. The resistance began to decrease above  $V_G = 22$  V, approximately corresponding to the  $V_{th}$ . In the characteristic features, the magnitude of resistance reduction rate increases with increasing  $V_G$  and the initial reduction speed is faster in the larger  $V_G$ , while the reduction speed became slower with time.

To understand such transport behaviors in a variety of  $V_G$ , theoretical investigations have been carried out with a combination of chemical reaction kinetics at the interface and ion diffusion model under an electric field<sup>32</sup>. The external hydrogen ions stochastically react with VO<sub>2</sub> at the interface. The reaction rate depends on the external hydrogen ion concentration ( $n_{H^+}$ ) generated by electrolysis of the absorbed water. The  $n_{H^+}$  tends to increase with increasing current between the gate and channel electrodes ( $I_{gc}^{ER}$ ), promoting formation of HVO<sub>2</sub>. While at the same time, desorption of hydrogen, namely return to VO<sub>2</sub>, would occur because of the natural recovery of resistivity by the thermal energy as seen in Supplementary Information section E. Thus assuming the reversible reaction, the time evolution-dependence of the concentration of intercalated ions inside VO<sub>2</sub> at the interface ( $n_{inter}$ ) can be written as a differential equation with respect to time ( $t$ ):

$$\frac{dn_{inter}}{dt} = k_1 n_{H^+} - k_2 n_{inter} \quad (1)$$

where  $k_1$  and  $k_2$  are the forward and reverse reaction rate constants, depending on the activation energy at the interface and temperature. Next, we consider how the intercalated ions diffuse in VO<sub>2</sub>. Theoretically, for ion diffusion, the ionic fluxes likely arise from the gradients of the ion concentration and the electric gradients in solid-state materials<sup>32</sup>. Thus, as  $n_{HVO_2}$  is the hydrogen ion concentration in VO<sub>2</sub>, the hydrogen ion flux ( $J_{HVO_2}$ ) can be described as:  $J_{HVO_2} = -D\nabla n_{HVO_2} + \mu E n_{HVO_2}$ , where  $D$  is the diffusivity,  $\mu$  is the mobility and  $E$  is the internal electric field in VO<sub>2</sub>. The first and second terms represent ion diffusion by the ion concentration gradient and by an electric field, respectively. The  $E$  resulting from  $V_G$  is screened by mobile electrons in VO<sub>2</sub> according to Poisson's equation, given as a function of the distance ( $x$ ) from the interface ( $x=0$ ), namely,  $E(x) = \frac{eN_0}{\epsilon_0\epsilon_r}(x_0 - x)$ , where  $e$  is the elementary charge,  $N_0$  is the carrier density in VO<sub>2</sub>, and  $\epsilon_r$  and  $\epsilon_0$  are the relative permittivity of VO<sub>2</sub> and the permittivity of a vacuum, respectively.  $x_0$  can be expressed as:  $\frac{\epsilon_0\epsilon_r V_G}{eN_0 d}$  as a function of  $V_G$ , where  $d$  is the distance between the gate and channel.  $N_0$  and  $\epsilon_r$  change with depending on the magnitude of intercalated hydrogen ions, however,  $N_0/\epsilon_r$  can be treated as a constant value because the change rate of  $\epsilon_r$  is roughly proportional to that of  $N_0$ <sup>33</sup>. Thus, the length of  $x_0$  would be determined only by the magnitude of  $V_G$ , and  $E$  linearly decreases as a function of  $x$  and become zero at  $x_0$ , as shown in Fig. 4a. To conduct the unsteady state analysis, we use Fick's second law in the one dimensional case, namely,  $\frac{\partial n_{HVO_2}}{\partial t} = -\frac{\partial J_{HVO_2}}{\partial x}$ , which predicts the time and spatial evolutions of the ion concentration. With this the following equation was obtained:

$$\frac{\partial n_{HVO_2}}{\partial t} = -D \frac{\partial^2 n_{HVO_2}}{\partial x^2} + \frac{e\mu N_0}{\epsilon_r \epsilon_0} \{n_{HVO_2} - (x_0 - x)\} \frac{\partial}{\partial x} n_{HVO_2} \quad (2)$$



**Figure 4. Simulated transport properties determined by the diffusion of intercalated ions.** (a) Schematic of the ion intercalation at the interface between air and VO<sub>2</sub>, resulting from chemical kinetics and the diffusion area (gray region), found using Fick's diffusion model under an electric field ( $E(x)$ ) derived by Poisson's equation. The simulated channel resistance was calculated using the parallel resistor model for the intercalated ( $\rho_{IH}^i$ ) and non-intercalated ( $\rho_0$ ) resistivities and by taking each width into consideration, as shown on the right side in (a). (b) Time dependence of the simulated  $R/R_0$  with a variety of  $V_G$  values for 500 nm wide VO<sub>2</sub> channels. (c,d) Spatial- and time-evolution maps of the hydrogen ion concentration at (d)  $V_G = 27$  V and (e) 38 V.  $x = 0$  indicates the interface.

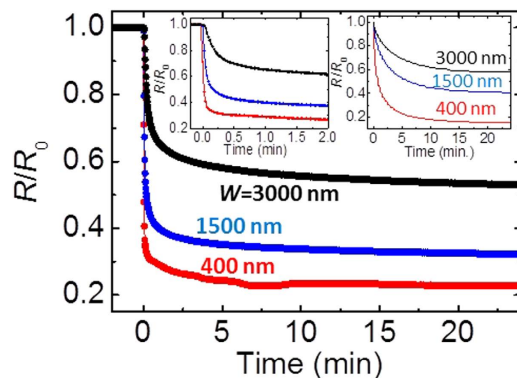
Furthermore, using a parallel resistor model for the resistivity in the intercalated ( $\rho_{IH}^i$ ) and non-intercalated ( $\rho_0$ ) parts in Fig. 4a and assuming a 1% hydrogen intercalation per VO<sub>2</sub> unit cell induces one order of magnitude reduction in the resistivity<sup>17,18</sup>,  $R/R_0$  could be evaluated as the following equation:

$$\left(\frac{R}{R_0}\right)^{-1} = \left[4 \frac{x_0}{m} \sum_{i=0}^m \frac{1}{\rho_{IH}^i} + (w - 4x_0) \frac{1}{\rho_0}\right] \times \frac{\rho_0}{w} \quad (3)$$

where  $\rho_{IH}^i$  is the part of the spatially divided resistivity in the diffuse area taking  $2 \times x_0$  in consideration of ion diffusion by the ion concentration gradient, which is divided into  $i$ , and is given as:  $\rho_0 \times 10^{-n_{HVO_2}^i}$ , where  $n_{HVO_2}^i$  represents the hydrogen concentration in segment  $i$  ( $i$ : integral), derived using the finite difference method in equation (2) and the boundary conditions in equation (1). A more detailed derivation is outlined in the Supplementary Information section F.

The experimental results in Fig. 3 are significantly reproduced in Fig. 4b as  $k_1$ ,  $k_2$  and  $\mu$  are fitting constants, though the more perfect reproduction requires more consideration efforts in the setting parameters, for example, considering  $k_1$  and  $k_2$  parameters depending on  $V_G$ , which make enhanced the reduction rate of resistivity with increasing  $V_G$ , and more precise resistive simulation like a random resistor network. Furthermore, this simulation enough includes the important essence of ion diffusion behavior, time and spatial evolutions of the ion diffuse in VO<sub>2</sub> are shown in Fig. 4c,d, which are in the cases at  $V_G = 27$  and 38 V, respectively, where  $x = 0$  indicates a channel edge. Hydrogen ions expand with time and the concentration increase with increasing  $V_G$ . Within the frame work of this model, interestingly, hydrogen ions accumulate in an inner area, clearly observed at  $V_G = 38$  V in Fig. 4d. This is caused by the continuous non-equilibrium states of the ion intercalation and diffusion by an electric field. In more detail, this accumulation is induced by the slower ion-diffusion rate in the inner part, depending on deduction of internal electric field with increasing  $x$ . As a token of this scenario, following the removal of any  $V_G$ , this accumulation fades away in time due to the ion-diffusion by concentration gradient and finally the concentration become homogeneous and equilibrium states. This diffusion behavior at  $V_G = 0$  is significantly reproducible for the persisting resistance decrease even after removal of the  $V_G$  in Fig. 2a, shown by the simulation in Supplementary Information section G. Thus this device suggests to be a kind of proton pumps in solid-state system.

**Drastic resistance modulation in narrower nano-channel.** Moreover, this model predict that the magnitude of resistance reduction rate enhance with decreasing the channel width ( $w$ ) because the effect on the interface diffusion due to the electrochemical gating from lateral sides become more prominent



**Figure 5. Enhancement of  $R/R_0$  with decreasing  $w$ .** Time dependence of the simulated  $R/R_0$  values for 400 nm, 1500 nm and 3000 nm wide  $\text{VO}_2$  channels at  $V_G = 100$  V. The left and right insets show the magnified view of Fig. 5 and the simulation results, respectively.

in narrower  $w$ . Figure 5 shows the time dependence of  $R/R_0$  with a variety of wire widths ( $w = 400, 1500$  and  $3000$  nm) at  $V_G = 100$  V and  $300$  K. The saturation values for  $R/R_0$  were enhanced with decreasing  $w$  and the sharpness of the resistance deduction in the initial process differs among the three devices as seen in the left inset of Fig. 5, magnified view from 0 to 2 minutes of Fig. 5. This behavior is in agreement with the simulation in the right inset of Fig. 5. Thus the further narrower channel will provide perfect electrochemical gating causing metal-insulator transition in whole channel area.

## Discussion

These results show that an air nanogap significantly works as an electrochemical reaction field, even in a gaseous atmosphere, and it is expected that the intercalated elements have an impact on reversibly changing in the physical properties of  $\text{VO}_2$ . This interfacial effect was more enhanced in smaller nanoscaled channels. This offers a new way to both investigate the fundamental physical properties on the effect of intercalation and non-equilibrium ion diffusion for a wide range of materials and may lead to the realization of new gas-sensing, storage applications and also ion pumps in solid-state materials.

## Methods

**Thin film growth.** 35-nm-thick  $\text{VO}_2$  films were prepared on  $\text{Al}_2\text{O}_3(0001)$  single crystal substrates by pulsed laser deposition using an ArF excimer laser at  $450^\circ\text{C}$  under an oxygen pressure of  $1.0$  Pa. Using X-ray diffraction measurements, it was confirmed that the films were  $b$ -axis-oriented without any impurity phases.

**Device fabrication.** The films were patterned into nanowire channels with planer-type field gates by nanoimprint lithography and reactive ion etching using  $\text{O}_2$  and  $\text{SF}_6$  gases. As advantages of this method, we can easily obtain  $200$  nm to  $400$  nm-air gaps between  $\text{VO}_2$  gate electrodes and  $\text{VO}_2$  channels, and fabricate many PG-FETs at one process. Also, since the resistivity of  $\text{VO}_2$  is roughly  $1$  ohm cm even in insulating region at room temperature,  $\text{VO}_2$  gate should enough work as gate electrodes in electrostatic effect. Pt/Cr electrodes were deposited by radio-frequency sputtering. Ohmic contacts between the  $\text{VO}_2$  films and electrodes were confirmed.

**Electrical measurements.** The transport characteristics were measured using a two terminal method with a Keithley 2635A.  $V_G$  was applied using a Keithley 236 and the currents between the gate and source electrodes were monitored simultaneously. The temperature of the device was controlled by a Peltier-based temperature stage (T95, Linkam). The gaseous conditions, from dry air to  $80\%$  humidity were controlled in a glovebox. The humidity fluctuation was within  $\pm 2\%$ .

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## Author Contributions

T.S. fabricated the devices, conducted the measurements and analyzed the data. H.U. contributed to the nanofabrication processes used to prepare the devices and the experimental setup. T.K. and H.T. planned and supervised the research. T.S., T.K. and H.T. wrote the manuscript. All authors discussed the results.

## Additional Information

**Supplementary information** accompanies this paper at <http://www.nature.com/srep>

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